Preprint
UCRL-JC-144283

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J. J. Haslam, M. A. Wall, D. L. Johnson, D. J. Mayhall, A. J. Schwartz

This article was submitted to
2001 Materials Research Society Fall Meeting, Boston, MASS., November 26-30, 2001

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

November 14, 2001

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

Phase Transformation Hysteresis in a Plutonium Alloy System: Modeling the Resistivity during the Transformation

Jeffery J. Haslam, Mark A. Wall, David L. Johnson, David J. Mayhall, and Adam J. Schwartz
Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550

ABSTRACT

We have induced, measured, and modeled the $\delta - \alpha'$ martensitic transformation in a Pu-Ga alloy by a resistivity technique on a 2.8-mm diameter disk sample. Our measurements of the resistance by a 4-probe technique were consistent with the expected resistance obtained from a finite element analysis of the 4-point measurement of resistivity in our round disk configuration. Analysis by finite element methods of the postulated configuration of α' particles within model δ grains suggests that a considerable anisotropy in the resistivity may be obtained depending on the arrangement of the α' lens shaped particles within the grains. The resistivity of these grains departs from the series resistance model and can lead to significant errors in the predicted amount of the α' phase present in the microstructure. An underestimation of the amount of α' in the sample by 15%, or more, appears to be possible.

INTRODUCTION

Plutonium and its alloys have the distinction of producing 6 allotropic phases between room temperature and the liquid state [1]. In pure plutonium the δ phase is stable between 325 and 460°C. However, the δ phase can be stabilized (to a metastable state) at room temperature by additions of various alloying elements. These alloying elements include Al, Ce, Ga, In, Zn and others [1]. In particular, the δ to α' phase transition is unique in having what is believed to be a martensitic type phase transformation with a nominally 20% change in density resulting from the transformation. This transformation has a large hysteresis in the forward and reverse directions and has been observed to have an isothermal characteristic even though it is believed to be martensitic [2,3]. The large volume change during the transformation probably leads to considerable plastic deformation to accommodate forming particles of the α' phase. This is thought to make a significant contribution to the rather large hysteresis in the transformation.

Dilatometry has been used to characterize the δ to α' phase transformation [2-4]. The hazards and difficulties associated with working with Pu metal make it necessary and useful to work with very small quantities of the material. The sample size available to this project was a disk, 2.8-mm in diameter and less than 500μm thick (a standard TEM foil size before thinning for electron transparency). Although other dilatometry techniques might be possible, we have chosen resistivity to characterize the martensitic transformation in this plutonium alloy. Resistivity has been used previously to measure phase transformations in plutonium [2,5], and more particularly has been used to follow the δ to α' phase transformation in alloys of δ-Pu stabilized by the addition of Al or Ga. [6,7]. However, our sample shape did not allow for a standard resistivity measurement arrangement. Therefore, we performed a model analysis of resistivity with a disk sample geometry and compared this with actual resistivity measurements.

The phase transformation is readily detectable with resistivity because the α' phase has a resistivity that is approximately 45% greater than the δ phase at room temperature and continues to remain significantly greater than that of δ over the temperature range where the forward and reverse transformations occurred [1]. The usual interpretation of the resistance data during the transformation is to apply a linear approximation to the amount of α' formed based on the difference between the resistivity of the pure α and pure δ materials [3,5]. The linear approximation basically represents the microstructure during the transformation in terms of a connection of the alpha and delta phase regions as resistors in series. However, we believed that the series resistance approximation might underestimate the amount of transformation in the sample because the α' particles are dispersed as lens or lenticular shapes within the δ grains.

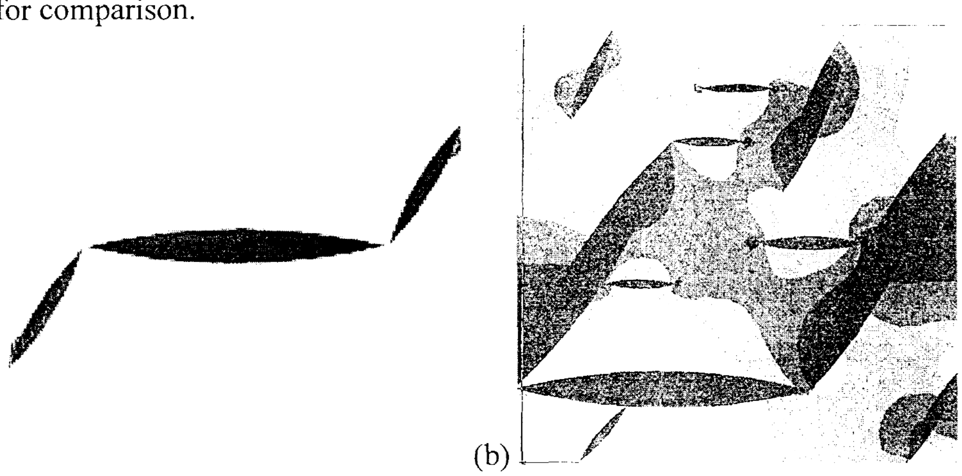
EXPERIMENTAL

Resistivity measurements were made in a 4-probe or Kelvin resistance measurement technique. Wires were used for contacts to one circular face of the disk sample and arranged along a diameter of the sample. The wires were placed parallel to each other on the surface and the spacing distances perpendicular to the wires were 0.330, 1.930, and 0.330 mm, respectively. The outer wires were used for the current probes and the inner wires were used to sense the voltage drop across the sample. To determine the resistivity of this disk shaped sample configuration, a finite element analysis package (Maxwell 3D Field Simulator, Version 5, Magnetostatic DC Conduction Module, Ansoft Corporation) was used to calculate the effective width of the circular sample to obtain an absolute resistivity measurement. The finite element analysis indicated that the current spreads rather uniformly between the inner (voltage) probes and through the sample thickness with some perturbations at the locations of the current and voltage probes. The effective width that was calculated was 1.8853 mm for typical properties of the sample and it was observed that the effective width varied 0.5% or less for expected variations in the resistance of the sample. At most, a 2% error is possible with misalignment of the electrical probes on the sample, but this would be a relative error only since it is expected the probes would not move during the experiments.

Figure 1. Optical Microscopy - Nomarski interference contrast. White and black elongated particles are α'. Isothermal hold at –118°C, 1000 seconds.

Figure 1 shows a micrograph illustrating the lens-like shape of the α' particles that formed within the delta grains. To better understand the relationship between results from resistivity measurements during the $\delta - \alpha$' phase transformation and volume fraction of α', an analysis of the changes in resistivity from some postulated model grains with particles of α' was performed. This approach was an approximation limited to a two-dimensional analysis of lens shaped α' phase particles within a square grain of δ. The resistance of these model grains was used to produce an array of randomly transformed grains, which could be analyzed as a resistor network with conduction through all four sides.

The modeling of resistivity of the grains used the same software mentioned above. Some examples of these configurations are shown in Figure 2. The resistance of a network of 100 square grains (10 x 10 array) was determined by analyzing a network of resistors associated with the grains. The orientation of the grains within the network were assigned randomly unless otherwise constrained by the analysis. Grain orientations of 0° and 90° were possible. The amount of α' in the grains as well as the number of δ grains containing α' was also assigned randomly. The resistance was calculated between top and the bottom of the 10 by 10 array of grains with the top and bottom edges having an equal potential along their length. The two sides of the array were connected so that effectively the composite of the 100 grains was a thin wall tube. A Gauss-Seidel iteration was used to obtain the resistance of the network. The resulting resistance was used to calculate a volume fraction of α’ that would be expected if the series model for resistivity was assumed. The actual volume fraction of α’ in the simulation was recorded for comparison.



(a) (b)

Figure 2. (a) Thin lens α’, (b) 11 lens configuration of α’. Dark lens shapes are the α’. Other contours reflect current density.

RESULTS AND DISCUSSION

Resistivity measurements of the transformation obtained using 4-probe resistivity measurement on the disk sample are plotted in figure 3. These results are qualitatively quite similar to previous work [6,7]. Optical microscopy, figure 1, confirmed similar observations made by others [8] of the lens shaped features of the α’ phase within the δ microstructure of the plutonium alloy. The delta phase grains are observed to contain certain preferred orientations, or variants of the α’. Up to three oriented variants are typically observed in a planar section. One of these variants can often dominate in terms of volume fraction over the others. Thus, an orientation dependence of the resistivity of the microstructure can be relevant for the determination of the amount of α’ phase present. In the plots, the difference between the amount of α’ phase in the simulation and the amount of α’ that would be assumed to be present from the series resistance approximation is plotted against the amount of α’ in the simulation in figures 4 a) – c).

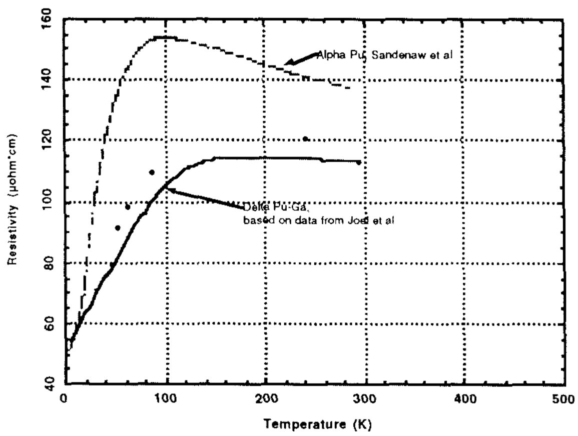
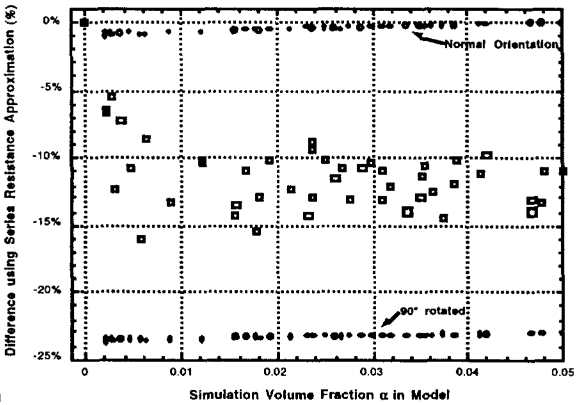
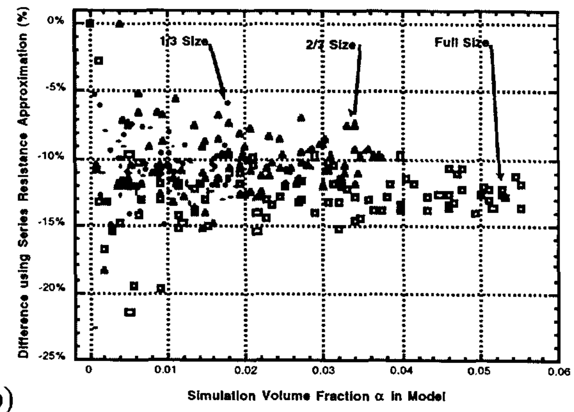


Figure 3. Resistivity measured on a Pu-Ga alloy using 4-probe resistivity on a disk sample.

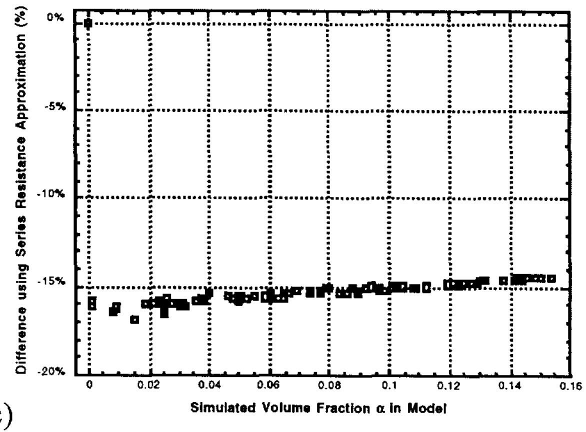
In figure 4 a), the comparison of error with random orientation for a grain with 3 lens shaped α' phase particles in the δ grain shows that the underestimation in the amount of α' is significant. The two additional sets of data in the figure show the difference from the series resistor model when all the grains containing the α' are forced to have one or the other orientation. In this case, the scatter in the results is significantly smaller. The random orientation of the transformation within the grains apparently contributes significantly to the scatter. The scatter is also produced by both the statistical probability associated with the clustering of transformed grains near each other and the blocking of current flow by rows of adjacent grains transforming. In this particular simulation, there is considerable difference in the resistivity in the vertical and horizontal directions. When random probability allows for more grains of one orientation to form in the array, variations from the average are observed. It is expected that with a larger network of grains (resistors in the model) this scatter might converge. It is also observed that when very few grains contain α' particles and consequently statistically the majority of the grains could have similar orientations, or be clustered near each other, anomalously large or small differences can occur between the volume fraction of α' in the simulation and amount of α' determined using the series approximation.



a)



b)



c)

Figures 4. Difference between simulation and series resistance model.

It is also apparent that simulations with a larger fraction of the grains containing α' particles make the difference between the simulation and the series model decrease. When a larger fraction of the grains in the array contain the α' particles, there is a greater tendency for uniformity in the distribution of transformed grains and consequently the higher resistances of the transformed grains are more likely to have a larger contribution to the overall resistance. As mentioned earlier, having anisotropic resistivity in a grain is a relevant issue to this work because it is often observed that one directional variant comprises a substantial amount of the α' present in a δ grain that partially transforms.

Figure 4 b) shows the results for analyses of grains that have one-third and two-thirds of the amount of α' as that in the grains from figure 4 a). These are approximations to a transformation process with the α' particles growing within the δ grain. For these grains, the α' particles were taken to expand from their center. This may not, however, be an accurate approximation since α' particles have been observed to nucleate from grain boundaries and from other α' particles. The small differences in the results for the 1/3 and 2/3 lens sizes compared to the full size lenses can be attributed to the actual differences measured in the resistivities of these model grains. In this case, the resistivity for these model grains scale with the amount of α' phase within the grain although the overall average resistance (from both the horizontal and vertical directions) is still significantly lower than that obtained from the series model.

Figure 4 c) shows a case where a δ grain contains 11 α' lenses that are fairly uniformly distributed throughout the grain. In this simulation, it turned out that the resistivities in the two directions were nearly equal. Consequently, the scatter in the plot was rather small for this simulation. It is however, clear that the resistivity of the δ grain containing the α' particles, is a major factor in the difference from the series model approximation for the amount of α'. In this case the grain with 11 lens shaped α' phase particles in the δ grain had a resistivity that was about 14% less than what would be predicted by a series resistor model. A better relationship between the resistance measured during δ to α' transformation and the amount of α' present in the microstructure will be possible when more accurate configurations of α' particles in the delta grains can be determined. Following this approach should allow some reasonable comparisons between results from dilatometry, image analysis, and resistometry, which is a future goal of this effort.

SUMMARY

We have followed the progress of the δ to α' phase transformation in a Pu-Ga alloy by a resistivity technique, using a 2.8 mm disk sample and a 4-probe arrangement. Our measurements of the resistance are consistent with the resistance calculated from a finite element analysis of a 4-probe resistance measurement with the probes arranged on a disk sample. Analysis by finite element methods of the postulated configuration of α' phase particles within model δ grains suggests that a considerable anisotropy in the resistivity may occur depending on the arrangement of the lens shaped α' particles within the δ grains. The resistivity of these grains departs from the series resistance model and can lead to significant differences in the amount of predicted α' phase present in the microstructure. An underestimation of the amount of α' in the sample by as much as 15%, or more, appears to be possible.

An important factor in relating the actual amount of α' present in a sample by a resistivity technique is the resistivity of the microstructure produced in the grain rather than just the resistivity of the new phase. Anisotropy or orientation effects in the effective resistivity will be averaged out in the sample if the dimensions of the test sample are large enough. There will also be a minor effect due to the number fraction of grains that contain transformed particles. The resistance is slightly lower in those samples with smaller number fractions of grains with particles because each grain is effectively a resistor in a resistor network that allows for considerable parallel circuit paths. This effect is diminished as the amount of δ grains containing the α' particles approaches 100% or if all the δ grains transform to a similar extent concurrently. In both cases, the transformed grains will more uniformly fill the sample microstructure.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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